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Interactions in solution between a hydrophobic polymer and various kinds of surfactants

E. Kientz and Y. Holl

Institut Charles Sadron (EAHP-CRM), Centre National de la Recherche Scientifique et Université Louis Pasteur, Strasbourg I, France

Abstract: Interactions in solution between a hydrophobic polymer and surfactants were studied by viscometry, light scattering and conductimetry measurements. One polymer, poly(2-ethyl hexyl methacrylate) (P2EHMA), five surfactants, sodium dodecyl sulfate (SDS), hexadecyl trimethylammonium bromide (HTAB), hexadecyl pyridinium chloride (HPCl), and ethoxylated nonyl phenol containing 10 or 25 segments of ethylene oxide (NP10 or NP25), and one solvent mixture, THF/6 vol% H_2O were used in this work. For the P2EHMA/surfactant mixtures in THF/6 vol% H_2O, the viscosity versus surfactant concentration curves are similar in shape for all surfactants. They show a minimum at low surfactant concentration followed at higher concentration by a maximum and a plateau. An interpretation of these curve shapes is proposed. The relevance of these findings to the problem of the polymer/surfactant interactions in latexes and latex films is also discussed.

Key words: Hydrophobic polymer/surfactant interaction – viscometry – poly(2-ethyl hexyl methacrylate) – sodium dodecyl sulfate (SDS) – hexadecyl trimethylammonium bromide (HTAB) – hexadecyl pyridinium chloride (HPCl) – ethoxylated nonyl phenol (NP10 or NP25).

Introduction

Latex film properties have been studied in our laboratory for several years. These properties, like adhesion to various supports, mechanical strength, and permeability are strongly influenced by the distribution of the surfactant in the film thickness. For example, if the surfactant tends to concentrate at the film-support interface, adhesion may be seriously damaged by the constitution of a weak boundary layer [1]. This is the reason why the distribution of surfactants in latex films is extensively studied [2–8]. The concentration profile of the surfactant in the film thickness depends on the polymer-surfactant interactions as shown, for instance, by Urban et al. in the dioctylsulfosuccinate/poly(ethyl acrylate-co-methacrylic acid) system [2]. These interactions are thus very important to investigate. Several possibilities of interactions, of various intensities depending on the particular system, exist between polymers and surfactants (electrostatic, dipolar, hydrophobic, London, . . .). The question is complex and requires careful analysis. We tried to study polymer-surfactant interactions through the adsorption characteristics of surfactants onto the surface of latex particles and the determination of adsorption free energies [7, 8]. This article describes our attempt to go a step further and study polymer-surfactant interactions in solution, in order to see whether the information obtained in this situation are relevant to the problem of polymer-surfactant interactions in latexes or latex films.

Interactions in solution between polymers and surfactants have been often investigated because of the importance of systems containing both products in many applications like paints, pharmaceuticals [9], oil recovery [10], etc. An important point to stress first is that in all publications we could find in the literature so far, the solvent was water. Only water-soluble polymers like polyvinylpyrrolidone (PVP), poly(ethylene oxide) (PEO), poly(vinyl alcohol) (PVA) [or poly(vinyl alcohol-co-vinyl acetate) with low vinyl acetate content], and polysaccharides were studied. All results reported indicate the occurrence of some kind of interaction, whatever the type of surfactant, giving rise to modifications of the properties of the pure polymer or surfactant solutions detected at even low concentration by techniques like tensiometry [11, 12], viscometry [13–17], dialysis [12, 18], NMR [19, 20], fluorescence [21], and neutron scattering [22]. In general, anionic surfactants interact more strongly with nonionic polymers like PVP or PEO than do cationic surfactants [23, 24]. In all cases, the interactions are increased when the hydrophobicity of the polymer increases [25]. Strong electrostatic attractions occur between polyelectrolytes and oppositely charged surfactants [26]. Depending on the particular polymer-surfactant system and on the surfactant concentration, the surfactant may adsorb onto the polymer in the form of individual molecules or small aggregates or in the form of micelles. Mixed micelles may be formed with surfactant molecules and polymer segments. This was shown by NMR and neutron scattering by Cabane [19, 22] and confirmed by fluorescence by Turro et al. [21] in the sodium dodecyl sulfate/PEO system where around 10% of the polymer segments are incorporated in mixed micelles. At high surfactant concentration, free surfactant micelles are the dominant species in the solution. An ionic surfactant adsorbed onto a nonionic polymer via its hydrophobic tail by hydrophobic interactions changes the nonionic polymer into a polyelectrolyte-like polymer, and electrostatic repulsions between the ionic heads of the surfactant molecules cause an expansion of the macromolecule easily detectable by viscometry [14, 15].

Latex films are mostly constituted of hydrophobic polymers. We were thus interested in polymer/surfactants system where the polymers are hydrophobic. This raises the problem of the solvent. It is often difficult to find a solvent common to the hydrophobic polymer and to the surfactant. In our work, solvent mixtures were used. The systems then contain four constituents, one polymer, one surfactant, and two solvents. This constitutes an additional difficulty, but is impossible to avoid. The main experimental technique for this work was viscometry, but some light scattering and conductimetry measurements were also performed. The particular systems investigated are the following. The polymer was a methacrylic homopolymer, poly(2-ethyl hexyl methacrylate) (P2EHMA). It was chosen because P2EHMA latexes form films at room temperature. Five surfactants were used, namely, sodium dodecyl sulfate (SDS), hexadecyl trimethylammonium bromide (HTAB), hexadecyl pyridinium chloride (HPCl), and ethoxylated nonyl phenol containing 10 or 25 segments of ethylene oxide (NP10 or NP25). The solvent was a tetrahydrofuranne (THF)-water mixture (6% H_2O by volume). These systems were compared to a previously investigated one [27], namely, the poly(methyl methacrylate-co-butyl acrylate) (45:55 wt%)/SDS in acetone/water (4% H_2O by volume).

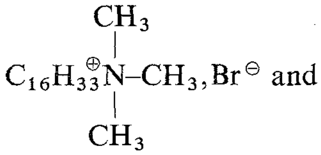
Experimental

Products

The polymer, poly(2-ethyl hexyl methacrylate) (P2EHMA) was synthesized by emulsion polymerization as described elsewhere [7, 8]. After coagulating the latex in ethanol, the polymer was purified by water rinsing and three cycles of solubilization in ethyl acetate and precipitation in distilled water. It was then dried in an oven at 65 °C for 48 h. M_w is usually very high for emulsion polymers, $7 \cdot 10^6$ g/mol for our P2EHMA.

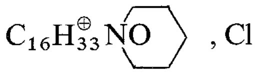
Five different surfactants were used in this work. – Sodium dodecyl sulfate ($SDS{:}C_{12}H_{25}SO_4^{\ominus}Na^{\oplus}$) is one of the most popular and most extensively studied surfactants. We used SDS supplied by Fluka with an initial purity of 98%. It was further purified by Soxhlet extraction in anhydrous diethyl ether [28]. Purity was assessed by studying the liquid-air interfacial tension as a function of surfactant concentration in water. The critical micellar concentration (CMC) was found at $2.68\ g \cdot l^{-1}$ (or $9.3 \times 10^{-3}\ mol \cdot l^{-1}$), which is close to the values reported in the literature for pure SDS [29]. The tensiometry curve showed only a weak minimum, $0.5\ mN \cdot m^{-1}$, at the CMC. The surfactant was thus considered as reasonably pure. Recrystallizations in absolute ethanol were not efficient at all with this particular product.

– Hexadecyl trimethylammonium bromide (HTAB)



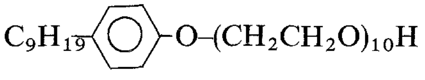
$C_{16}H_{33}\overset{\oplus}{N}(CH_3)_2$–$CH_3$, $Br^{\ominus}$ and

– Hexadecyl pyridinium chloride (HPCl)

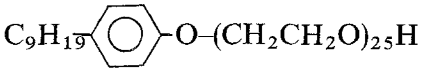


both supplied by Fluka (initial purity 99%), were purified by four times dissolution in absolute ethanol and recrystallization in anhydrous diethyl ether. No minimum was found in the surface tension versus concentration curve of both surfactants. The CMC was 0.33 g·l^{-1} (9.1×10^{-4} mol·l^{-1}) for HTAB and 0.34 g·l^{-1} (9.6×10^{-4} mol·l^{-1}) for HPCl [30]. For comparison, a few data concerning HPBr are also presented.

– Ethoxylated nonyl phenol (commercial name Rewopal) containing 10 or 25 segments of ethylene oxide (NP10 or NP25)



or



A minimum of 1 mN·m^{-1} in the tensiometry curve could not be eliminated. The polydispersity of the ethoxylated moiety was checked by HPLC in acetonitrile and GPC in THF. In the HPLC and GPC diagrams, only one peak was apparent and the M_w/M_n ratio measured by GPC was less than 1.1, confirming a narrow mass distribution.

Methods

Choice of the solvent

The solubility of the different products in the solvent mixtures was assessed visually. For the P2EHMA/surfactant systems, THF/H_2O mixtures were used as solvents. The nonionic surfactants (NP10 and NP25) were soluble in the mixtures whatever the water content. The cationic surfactants (HTAB and HPCl) were soluble when the water content was above 4 vol%. The concentration of polymer in the solutions was fixed at 0.4 g/l. By increasing the amount of water in THF, the solubility of P2EHMA decreased. At 8 vol% of water in the solvent mixture, the polymer was no longer soluble. On the other hand, SDS started to be soluble in the THF/H_2O mixtures above 4 vol% of water. At 6 vol%, the limit solubility of SDS in the mixture was 0.7 g/l (2.4×10^{-3} mol/l). The water content was thus fixed at 6 vol%.

Viscometry

Capillary viscosities were measured at 25 °C using either an Ubbelohde or an Ostwald-Fenske viscometer. The various solutions were prepared 24 h before taking any measurement. Specific, reduced, and intrinsic viscosities are considered in this work.

Specific viscosity

$$\eta_{sp} = (\eta - \eta_0)/\eta_0 \simeq (t - t_0)/t_0 \qquad (1)$$

with η and η_0 being the solution and pure solvent viscosities, respectively; t and t_0, the flow times in the viscometer of the solution and pure solvent, respectively.

Reduced viscosity $\quad \eta_{red} = \eta_{sp}/C \qquad (2)$

C being either the polymer (C_p) or the surfactant (C_s) concentration.

Intrinsic viscosity

of a Newtonian solution, limit of the reduced viscosity when the concentration tends towards zero

$$[\eta] = (\eta_{sp}/C)_{C=0} \, . \qquad (3)$$

Huggins and Flory–Fox equations were used. Let us recall them here.

Huggins

$$(\eta - \eta_0)/\eta_0 C = \eta_{sp}/C$$
$$= [\eta] + k_H[\eta]^2 C + \ldots \qquad (4)$$

k_H = Huggins constant, characteristic of the polymer-solvent interactions

Flory–Fox $\quad [\eta] = \Phi[\langle R_G^2 \rangle^{3/2}]/M_w \qquad (5)$

R_G = radius of gyration of the macromolecule, Φ = universal constant equal to 3.67×10^{23}.

Light scattering

Elastic light ($\lambda = 632$ nm) scattering measurements were performed on HPCl solutions in THF/6 vol% H_2O at 25 °C. The angles were 45°, 90°, and 135°. The surfactant solutions were centrifugated at 14000 rpm for 2 h before use. Complementary to elastic scattering, a few inelastic scattering measurements were also performed on HPCl solutions with concentrations below 10^{-3} mol·l^{-1}.

Conductimetry

Electric conductivities of HPCl solutions in THF/6 vol% H_2O, with or without P2EHMA, were measured using a Wayne Kerr B 905 conductimeter.

Results and discussion

Pure polymer in THF/6 vol% H_2O

Reduced viscosities of P2EHMA in pure THF and in THF/6 vol% H_2O are shown in Fig. 1. Straight lines are obtained in accordance with Huggins equation. Intrinsic viscosities are determined by extrapolation of these lines to zero polymer concentration; they are presented in Table 1 with the corresponding Huggins constants and radii of gyration. Adding water to THF degrades the quality of the solvent, which is not surprising taking into account the high hydrophobicity of P2EHMA [8]. THF/6 vol% H_2O, with a Huggins constant between 0.7 and 0.8, is close to a θ solvent. Accordingly, the radius of gyration of the macromolecule decreases from THF to THF/6 vol% H_2O. These results are similar to those obtained by Gargallo and Radic [31], who studied the influence of cosolvents on viscometric properties of PVP in aqueous and non-aqueous solvents.

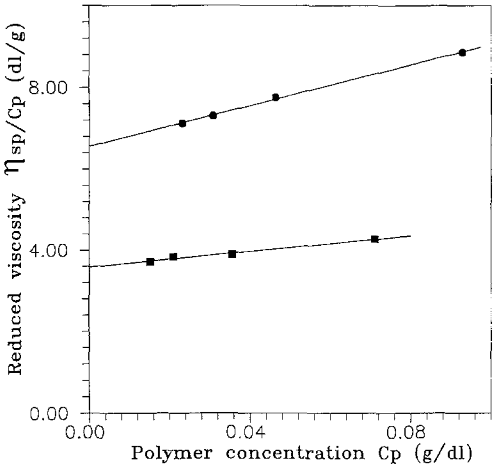


Fig. 1. Reduced viscosity η_{sp}/C_p versus P2EHMA concentration in THF (●) and in THF/6 vol% H_2O (■) at 25 °C

Table 1. Intrinsic viscosity [η], Huggins constant k_H, and radius of gyration R_G of P2EHMA in THF and in THF/6 vol% H_2O at 25 °C

Solvent	[η] (dl/g)	k_H	R_G (nm)
THF	6.55	0.58	23
THF/6 vol% H_2O	3.58	0.76	19

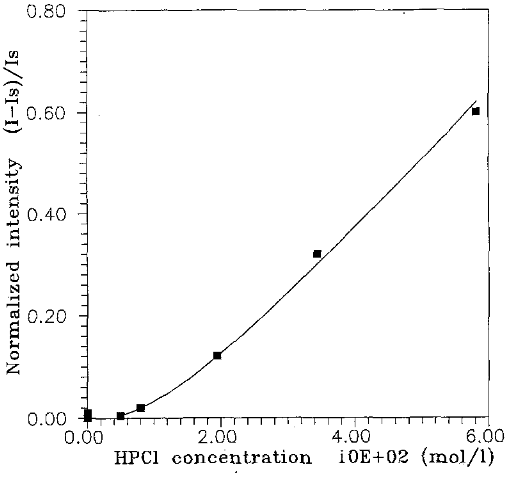


Fig. 2. Normalized intensity of scattered light at 90° versus HPCl concentration in THF/6 vol% H_2O. I intensity scattered by the solution; I_s intensity scattered by the pure solvent. Temperature 25 °C

Pure surfactants in THF/6 vol% H_2O

Figures 2 and 3 show the results of the elastic light scattering measurements performed on HPCl solution in THF/6 vol% H_2O. The normalized scattered intensity at 90° from the incident beam direction as a function of the surfactant concentration is presented in Fig. 2. Above a concentration of 5×10^{-3} mol·l^{-1}, scattering effectively occurs. However, the intensity of the scattered light is much less important than for an aqueous solution of HPCl. No surfactant

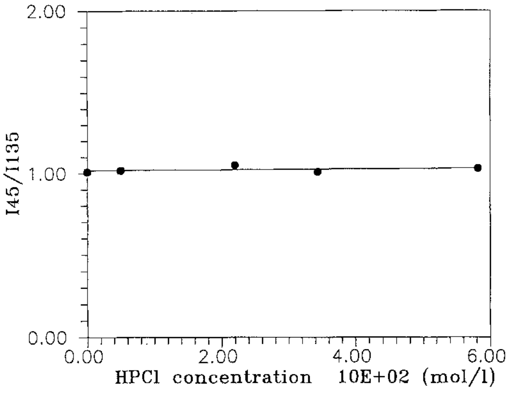


Fig. 3. Dissymetry factor I_{45}/I_{135} versus HPCl concentration in THF/6 vol% H_2O. I_{45} and I_{135}, intensity of the light scattered at 45° or 135°, respectively, from the incident beam direction. Temperature 25 °C

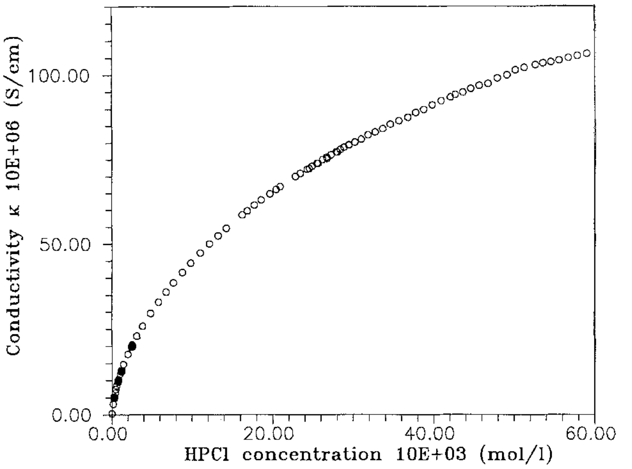


Fig. 4. Electric conductivity κ of HPCl solutions in THF/6 vol% H_2O versus concentration. (○) in the pure solvent; (●) in the solvent containing 0.40 $g \cdot l^{-1}$ of P2EHMA. Temperature 25 °C

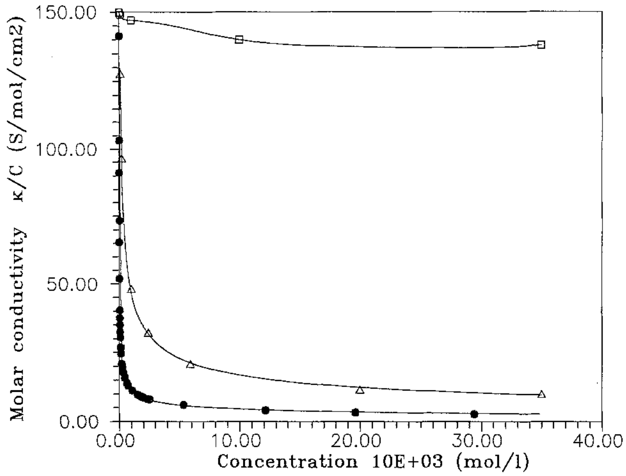


Fig. 5. Molar conductivity ($\Lambda_m = \kappa/C$) versus concentration for HPCl in THF/6 vol% H_2O (●), CH_3COOH in water (△), and KCl in water (□) at 25 °C. Data for CH_3COOH and KCl from ref. [33]

aggregates could be detected by inelastic light scattering at concentrations below 10^{-3} $mol \cdot l^{-1}$. The dissymmetry factor, I_{45}/I_{135}, is very close to 1, at all surfactant concentrations measured (Fig. 3). This indicates the presence of spherical or quasi-spherical aggregates. In pure water, the dissymmetry factor is also equal to 1, HPCl forms spherical micelles in this concentration range [32].

The electric conductivity (κ) of HPCl solutions in THF/6 vol% H_2O increases monotonically with increasing concentration, with or without the presence of P2EHMA (0.40 $g \cdot l^{-1}$) (Fig. 4). In water, one would observe two straight lines with different slopes below and above the CMC (above the CMC, the slope decreases because some counter-ions remain attracted in the vicinity of the micelles). Addition of 0.40 $g \cdot l^{-1}$ of P2EHMA to the solution does not affect the measured conductivity at all. Figure 5 represents the molar conductivity ($\Lambda_m = \kappa/C$) versus the concentration of HPCl in THF/6 vol% H_2O. Λ_m is very low for the highest surfactant concentrations and increases rapidly for the most dilute solutions. This behavior is typical of a weak electrolyte like acetic acid. For a strong electrolyte, KCl for example, Λ_m remains almost constant over the considered concentration range (Fig. 5). The dissociation of HPCl in THF/6 vol% H_2O must be very low. It is always less than the dissociation of acetic acid which is around 10% in water at a concentration of 10^{-3} $mol \cdot l^{-1}$ [33].

The reduced viscosity of the cationic (Fig. 6) and non-ionic (Fig. 7) surfactants varies linearly with concentration in THF/6 vol% H_2O in the range 10^{-2}–10^{-1} $mol \cdot l^{-1}$. For concentrations below 10^{-2} $mol \cdot l^{-1}$, the viscosity is close to that of the solvent. SDS could not be studied in the same way because of its limited solubility. Table 2 summarizes all values of the intrinsic viscosity of the surfactants in THF/6 vol% H_2O. It is less by a factor of 100 than the intrinsic viscosity of P2EHMA in the same solvent (Table 1).

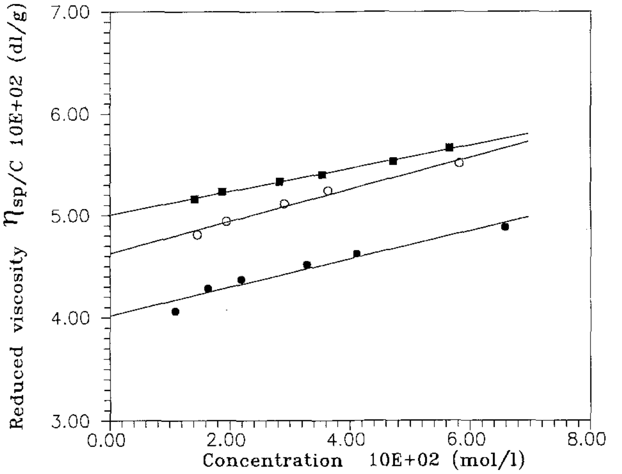


Fig. 6. Reduced viscosity η_{sp}/C versus surfactant concentration in THF/6 vol% H_2O for HTAB (●), HPCl (○), and HPBr (■) at 25 °C

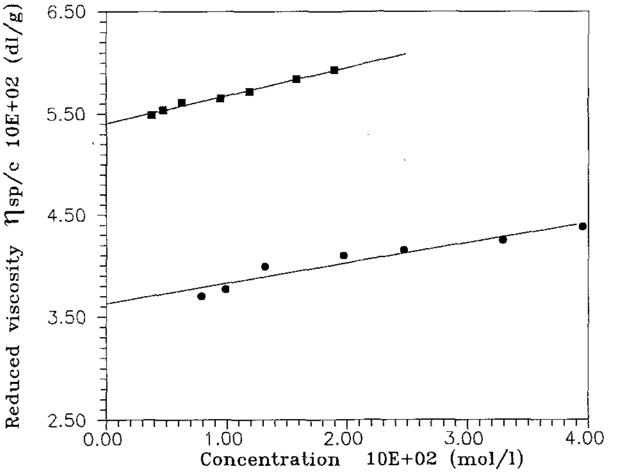


Fig. 7. Reduced viscosity η_{sp}/C versus surfactant concentration in THF/6 vol% H_2O for NP10 (●), and NP25 (■) at 25 °C

Surfactants have been studied far more in water than in non-aqueous solvents. For ionic surfactants, the aggregation number is usually much lower in organic media than in water and the CMC is often ill-defined. The aggregation takes place more progressively. When a CMC is apparent, it is higher than in water. Muller [34] has shown that cationic surfactants do not present a clear CMC in solvents having a low dielectric constant (benzene, CCl_4, . . .) and form aggregates containing 3 to 7 molecules, whereas sulfosuccinates have a better defined CMC and an aggregation number between 12 and 30. Reverse micelles are formed in organic solvents. This was shown, for example, by Amorin da Costa et al. [35] for HTAB in chloroform at concentrations around 0.3 $mol \cdot l^{-1}$. For non-ionic surfactants, the CMC is better defined and aggregation numbers are higher, although they do not reach values as high as in water [36, and references therein].

Table 2. Intrinsic viscosity of the cationic and non-ionic surfactants in THF/6 vol% H_2O at 25 °C

Surfactant	$[\eta]$ ($ml \cdot g^{-1}$)
HTAB	4.01
HPCl	5.00
HPBr	4.62
NP10	3.63
NP25	5.40

For HPCl in THF/6 vol% H_2O, elastic light scattering indicates the appearance of diffusing objects at a concentration of about 5×10^{-3} $mol \cdot l^{-1}$ (Fig. 2), whereas conductimetry curves do not exhibit a sharp slope change (Fig. 4). These results suggest a progressive aggregation process of HPCl in THF/6 vol% H_2O taking place above a concentration of 10^{-3} $mol \cdot l^{-1}$. The concentration of the apparent start of HPCl aggregation in THF/6 vol% H_2O (5×10^{-3} $mol \cdot l^{-1}$) is 5 times higher than the CMC in water (9.6×10^{-4} $mol \cdot l^{-1}$), which is not surprising in view of literature data.

To summarize this part, the behavior of HPCl in THF/6 vol% H_2O can be described in the following way. Below 10^{-3} $mol \cdot l^{-1}$, the surfactant is dissolved in molecular form. Above 10^{-3} $mol \cdot l^{-1}$, molecules progressively aggregate in small, spherical reverse micelles, most probably containing a certain amount of water inside. Furthermore, the counter-ion is very close to the ionic head of the molecule. The other surfactants of our series were not studied in the same manner. As an initial approach, we shall consider that they roughly behave similar to HPCl.

Polymer-surfactant mixtures in THF/6 vol% H_2O

The addition of increasing amounts of surfactant to a solution of P2EHMA in THF/6 vol%

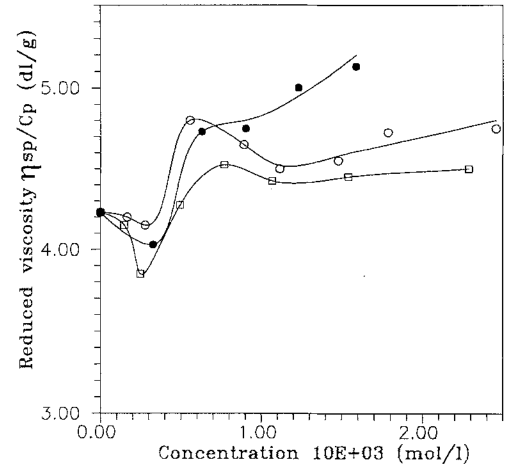


Fig. 8. Reduced viscosity η_{sp}/C_p of a P2EHMA solution in THF/6 vol% H_2O ($C_p = 0.40$ g/l) versus cationic surfactant concentration. Temperature 25 °C. (●) HTAB; (○) HPCl, and (□) HPBr

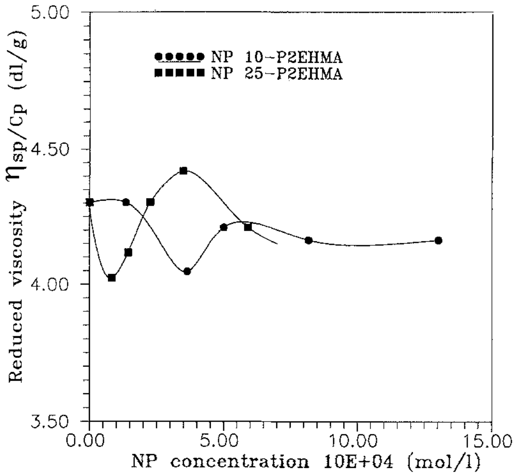


Fig. 10. Reduced viscosity η_{sp}/C_p of a P2EHMA solution in THF/6 vol% H_2O ($C_p = 0.40$ g/l) versus non-ionic surfactant concentration. Temperature 25 °C. (●) NP10; (■) NP25

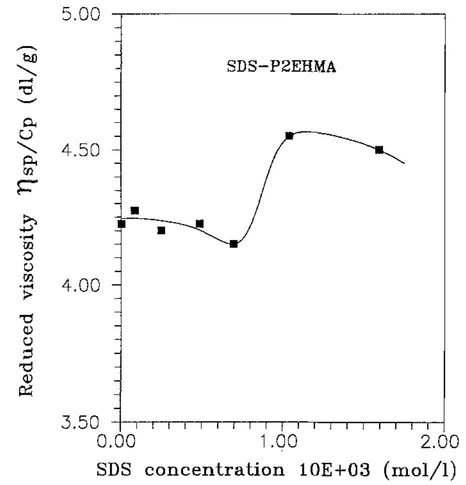
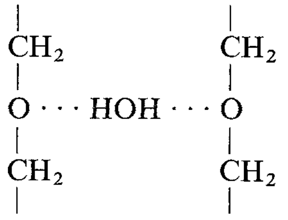


Fig. 9. Reduced viscosity η_{sp}/C_p of a P2EHMA solution in THF/6 vol% H_2O ($C_p = 0.40$ g/l) versus anionic surfactant concentration. Temperature 25 °C

H_2O (polymer concentration, C_p, $0.40\,g \cdot l^{-1}$) changes the reduced viscosity in the way shown in Figs. 8 (HTAB, HPCl, HPBr), 9 (SDS), and 10 (NP10 and NP25). The concentration range for the surfactants is 0 to $2 \times 10^{-3}\,mol \cdot l^{-1}$. For all surfactants, the curves look similar. First decreasing, η_{red} goes through a minimum, then it increases, goes through a maximum and reaches a plateau which can be slightly ascendant. The plateau is higher than the initial level of η_{red} (pure polymer) for the cationic surfactants and lower for the non-ionic ones. The positions and depths or heights of the minima and maxima and the start of the plateau depend on the nature of the surfactant.

The interpretation proposed for these curve shapes is the following. The first viscosity drop is due to the adsorption of the surfactant onto the polymer via its hydrophobic tail. As the ionic surfactants are only very weakly dissociated, their polar heads behave like dipoles which attract each other giving rise to a decrease of the hydrodynamic volume of the macromolecule. For the non-ionic surfactants, attraction occurs between the ethylene oxide segments, perhaps through hydrogen bonding involving a molecule of water as shown in the following scheme.



$$\begin{array}{ccc} | & & | \\ CH_2 & & CH_2 \\ | & & | \\ O & \cdots HOH \cdots & O \\ | & & | \\ CH_2 & & CH_2 \\ | & & | \end{array}$$

Another possibility is to simply invoke a decrease of the volume of the chain due to a diminution of the quality of the solvent when polar surfactant molecules are added.

By further addition of surfactant, the number of adsorbed molecules increases. Steric hindrance starts to take place, expanding the chains. The possibility also exits of a solvent quality effect. The polymer bearing dipolar surfactant molecules ressembles now a poly(zwitterion). Adding more surfactant in the medium results in an increase of the polarity of the solvent which can provoke an expansion of the chain. Such a viscosity increase was also observed by Galin et al. [37] in poly(ammonium sulfopropylbetaine) solutions by adding small zwitterionic molecules.

Then, a complete rearrangement of the adsorbed species may occur. The molecules could gather in the form of adsorbed micelles. Steric hindrance would decrease and, possibly, attractive London interactions between the hydrophobic tails of the surfactants could appear. This would explain the viscosity decrease after the maximum. The attractive London interactions between micelles could account for the fact that the viscosity at the plateau is less than the initial viscosity in the case of the non-ionic surfactants (Fig. 10).

In this interpretation, the start of the plateau would correspond to the saturation. Afterwards, the added surfactant would remain in the solvent, possibly in the form of free reverse micelles. These micelles would slowly increase the viscosity of the solution by their presence, but also by the fact that the reverse micelles would incorporate more and more water and thus the quality of the solvent in contact with the macromolecules would increase again as it would tend toward the characteristics of pure THF. The first possibility, increase of the viscosity by the mere presence of the micelles, is probably not dominant because the intrinsic viscosity of the surfactant is very low compared with that of the polymer (Tables 1 and 2).

A viscosity behavior of polymer/surfactant solutions similar to ours (viscosity drop at low surfactant concentration and then increase) was reported many years ago by Saito et al. [13, 16, 18] for PVP/cationic surfactant (octyl or dodecylammonium with counter-ions like SCN^- or I^-) or methylcellulose/SDS systems. The initial drop was interpreted by considering an adsorption of the surfactant onto PVP via the polar heads and attractive interactions between the hydrophobic tails which reduce the volume of the chains in solution. The case of methylcellulose/SDS was not discussed.

The P2EHMA/surfactant systems in THF/6 vol% H_2O can be compared with the poly(methyl methacrylate-co-butyl acrylate) (45:55 wt%)/SDS system in acetone/4 vol% H_2O studied in a previous work [27]. The difference is striking. The PMMA-BuA/SDS system behaves more classically. Viscosity immediately sharply increases, goes through a maximum and stabilizes. In acetone/4 vol% H_2O, the SDS is probably more dissociated than in THF/6 vol% H_2O because of a higher dielectric constant. If, for a first approximation, the dielectric constant of the mixture is calculated using

$$\varepsilon_m = X_{wat}\varepsilon_{wat} + (1 - X_{wat})\varepsilon_2$$

with ε_m dielectric constant of the mixture, X_{wat} volume fraction of water in the mixture, ε_{wat} dielectric constant of water, ε_2 dielectric constant of THF or acetone, a value of 11 is found for THF/6 vol% H_2O and 23 for acetone/4 vol% H_2O. SDS adsorbs onto PMMA-BuA and electrostatic repulsions between sulfate groups expand the chains. The maximum at higher surfactant concentration is explained, like in the previous system, by a rearrangement of the adsorbed species and the formation of adsorbed micelles. The plateau starts when adsorption is completed. This is confirmed by the shift towards higher surfactant concentrations when the polymer concentration increases [27]. The same viscometric behavior as for the PMMA-BuA/SDS system in acetone/4 vol% H_2O was observed before, for instance, for PVP/SDS in water by Saito [18] and Lopez de Sa [14] or PVP/SdeS (sodium decyl sulfate) by Lopez de Sa [15].

Is it possible, at this point, to extract more quantitative information from the data collected so far? It would be highly interesting to know the amount of adsorbed surfactant as a function of the amount of introduced surfactant (a kind of adsorption isotherm) and the intensities of the polymer-surfactant interactions. It would be satisfactory to be able to precisely interpret the differences in the curve shapes of the various surfactants, positions and heights or depths of the maxima or minima. At the moment, this kind of study is in a too early stage. The speculative interpretations presented above should first be confirmed by more data on other systems and by other techniques. Only then will it be possible to improve the knowledge of the hydrophobic polymer/surfactant systems in solution.

Conclusion

This work constitutes a first attempt to study hydrophobic polymer-surfactant interactions in solution. It was undertaken because of the importance of these interactions in the interpretation of the distribution of surfactants in latex films. The fact that the polymer is hydrophobic imposes the use of solvent mixtures which complicate the systems under investigation. The first steps are thus to study the behaviors of the pure polymer and pure surfactants in the solvent mixtures. The intrinsic viscosity of P2EHMA decreases by a factor of 1.8 from pure THF to the THF/6 vol% H_2O mixture. The intrinsic viscosities of the surfactants are around 100 times lower than the intrinsic viscosity of P2EHMA in THF/6 vol% H_2O. A light scattering and conductimetry study of HPCl in THF/6 vol% H_2O showed that, above 10^{-3} $mol \cdot l^{-1}$, molecules progressively aggregate in small, spherical reverse micelles and that the dissociation of the polar head of the surfactant is very weak. This study should be pursued to gain a better insight into the colloidal properties of HPCl in solvent mixtures and extended to the other surfactants of interest in this work. As far as polymer/surfactant mixtures in THF/6 vol% H_2O are concerned, a peculiar viscometric behavior was found. The viscosity versus surfactant concentration curves are similar in shape for all surfactants and show a minimum at low surfactant concentration followed at higher concentrations by a maximum and a plateau. Taking into account all our data and with the help of the knowledge of the literature on the subject, an interpretation of these curve shapes was proposed. A comparison with another system, PMMA-BuA/SDS in acetone/4 vol% H_2O, showed the dramatic influence of the dielectric constant of the solvent mixture on the viscometric results through its effect on the dissociation constant of the surfactant. All our interpretations are highly speculative. They should be confirmed by further work on these systems and other ones, using more sophisticated techniques like NMR and neutron scattering. More work would permit a better understanding of this important problem of the hydrophobic polymer/surfactant interactions in solution.

The study presented in this article is interesting in itself and in the prospects it opens. However, what is its usefulness in our field, the polymer-surfactant interactions in latexes and latex films? As long as the description remains qualitative, the aim is not attained. At least, a classification of the surfactants in the order of increasing or decreasing intensities of interaction with a polymer would be required. Furthermore, a polymer in solution does not behave like at a polymer/water interface or in the solid state. In particular, the conformational freedom of the chain in solution is much higher than in the solid state or at a polymer/water interface. This may strongly influence the adsorption characteristics of a surfactant onto the polymer. Adsorption studies of surfactants onto polymer particles directly performed in latexes [8] seem more promising, particularly the determination of adsorption free energies at the particle/water interface. Other ways of directly measuring the intensity of polymer/surfactant interactions should also be pursued.

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Authors' address:

Dr Y. Holl
EAHP
4, rue Boussingault
67000 Strasbourg, France